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The catalytic activity of new chiral salen complexes immobilized on MCM-41 by multi-step grafting in the asymmetric epoxidation

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Abstract

The chiral salen Mn(III) complexes were heterogenized on the siliceous MCM-41 by a new grafting method using (3-aminopropyl) trimethoxysilane and 2,6-diformyl-4-*tert*-butylphenol. The immobilized chiral salen Mn(III) complexes were stable during the reaction and exhibited a relatively high enantioselectivity for epoxidation of styrene and α-methylstyrene. © 1999 Elsevier Science Ltd. All rights reserved.

Chiral (salen) Mn(III) complexes have been found to be highly enantioselective for the asymmetric epoxidation of conjugated *cis*-disubstituted and trisubstituted olefins.[1–3] The increasing interest towards this reaction brought some authors to develop the heterogeneous chiral Mn(III) salen catalysts. However, to date three kinds of approach have been adopted for the immobilization of chiral salens: (1) the chiral salen complexes were supported on polymers by copolymerization of active groups in salen complex with styrene and divinylbenzene;[4] (2) the encapsulation of salen complex using ship-in-bottle method was applied,[5,6] and furthermore, (3) Mn salen ligands were immobilized by ion exchange reaction.[7,8] As introduced by some authors, most of the reported papers dealt with the immobilization method of chiral salen ligands only by the condensation of unsaturated olefin groups in salen structure with styrene and divinylbenzene or by impregnation. But the sequent anchoring method of reacting a functionalized ligand with reactive groups of organic and inorganic compounds (MCM-41), step by step, has not been reported yet. It is possible to synthesize various unsymmetrical chiral salens of different structure and to immobilize them onto inorganic supports such as MCM-41 and silica by this new multi-step grafting using diformylphenol as a buildiding block of salen structure. No attempt has been made to synthesize the grafted unsymmetrical salen complexes as in this work. Here we demonstrate the synthesis of the heterogenized chiral salen catalyst on the siliceous MCM-41 by a new grafting method using (3-aminopropyl) trimethoxysilane and 2,6-diformyl-4-*tert*-butylphenol. We also report herein that these new catalysts afford a high level of enantioselectivity in the epoxidation of unsubstituted olefins such as styrene and α-methylstyrene. For this study, the chiral salen complexes were synthesized and

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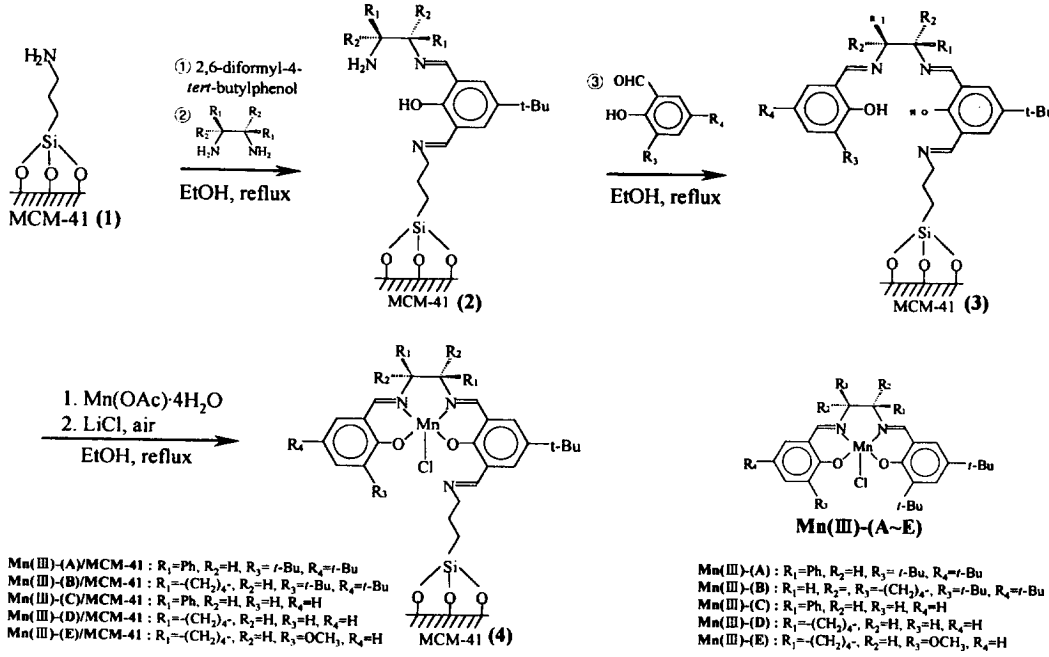
immobilized on MCM-41 by a grafting method according to the procedure shown in Scheme 1. In addition, homogeneous symmetrical and unsymmetrical chiral salen complexes of similar structure to the immobilized ones were synthesized and used as catalysts to compare the enantioselectivity in the epoxidation reaction.



Scheme 1.

The MCM-41 of very high crystallinity could be synthesized within 12 h by a modified evaporating method. The pore size of MCM-41 determined by N_2 adsosorption was 4.3 nm. This MCM-41 sample was used to immobilize the chiral salen complexes as shown in Scheme 1.

A suspension of 5.38 g of (3-aminopropyl) trimethoxysilane and 20 g of MCM-41 in 100 mL of toluene was heated to reflux with stirring. After heating for 6 h, 25 mL of solution containing methanol and toluene was distilled out from the mixture. The mixture was refluxed again for 6 h and cooled. The powder sample (**1**) was obtained in a 21.5 g yield after filtration and washing with diethyl ether. 2,6-Diformyl-4-*tert*-butylphenol was synthesized according to the procedure described by Chang et al.[9] Compound **1** was reacted with excess 2,6-diformyl-4-*tert*-butylphenol in refluxing ethanol for 10 h. After cooling, the powder was collected by filtration and washing with diethylether and methanol. This sample was dried in vacuum at 40°C. The immobilized chiral half unit (**2**) was synthesized by the condensation of powder sample obtained above and the available chiral auxiliary (1*S*,2*S*)-(+)-1,2-diphenylethylenediamine or (1*S*,2*S*)-(+)-1,2-diaminocyclohexane with excess amount in refluxing ethanol for 14 h. Compound **2** was collected by filtration, washing with methylene chloride and methanol, and drying in vacuum. 2,4-Di-*tert*-butyl salicylaldehyde was synthesized by the reaction of 2,4-di-*tert*-butylphenol (3 g, 14.54 mmol), tin(IV)tetrachloride (378 mg, 1.45 mmol), 2,6-lutidine (624 mg, 5.82 mmol) and *para*-formaldehyde (961 mg, 32 mmol) in a refluxed anhydrous toluene (30 mL) according to the procedure reported by Casiraghi et al.[10] The sample (**3**) was prepared by the condensation of 1.0 equiv. chiral half unit (**2**) immobilized on MCM-41 and 2.0 equiv. salicylaldehyde derivatives (2,4-di-*tert*-butyl salicylaldehyde or salicylaldehyde) in a refluxing ethanol for 18 h. Then, (salen) Mn(III) complexes immobilized MCM-41 (**4**) was readily accomplished by refluxing an ethanolic solution of a salen ligand with 2.0 equiv. of $Mn(OAc)\cdot 4H_2O$ and LiCl in air for 2 h, in sequence. The homogeneous symmetrical and unsymmetrical chiral salen

complexes (Mn(III)–(A–E)) of similar structure to the immobilized ones were synthesized to compare the enantioselectivity in the epoxidation reaction. The homogeneous unsymmerical salen complexes were synthesized by the condensation reaction of chiral half units with salicylaldehyde derivatives as shown by Lopez at al.[11] The epoxidation of unfunctionalized olefins was carried out with *m*-chloroperoxobenzoic acid (*m*-CPBA) as a terminal oxidant at 0°C and −78°C. The % ee values were determined by capillary GC using a chiral column (Astec, gamma-cyclodextrin trifluoroacetyl, 40 m×0.25 mm i.d.).

The trends in reactivity and enantioselectivity of the (salen) Mn(III) chloride complex immobilized on MCM-41 and the homogeneous complex of same structure in solution were examined for the epoxidation of styrene and α-methylstyrene. The result is shown in Table 1. Epoxidation reaction using a combined solution of *m*-CPBA/*NMO* was rapid both at 0°C and −78°C. The enantiosectivity and conversion were found to increase significantly at the low temperature. As shown in Table 1, a high % ee value was obtained particularly over more hindered catalyst such as Mn(III)–(A). Especially, the reaction using heterogenized Mn salen/MCM-41 of (A) and (B) gave a slightly improved selectivity as compared

Table 1
Epoxidation of styrene and α-methylstyrene using homogeneous and heterogenized Mn–salen complex as a catalyst

Entry	Substrate	Catalyst	Time	Temp(°C)	Ee(%) (a)	Conv.(%)
1	Styrene	Mn(III)-A	15min	0	65	75
2	Styrene	Mn(III)-A/MCM-41	2h	0	70	75
3	Styrene	Mn(III)-A/MCM-41	4h	-78	86	77
4	Styrene	Mn(III)-B	45min	-78	59	84
5	Styrene	Mn(III)-B/MCM-41	2h	0	53	71
6	Styrene	Mn(III)-B/MCM-41	4h	-78	65	73
7	Styrene	Mn(III)-C	45min	-78	84	97
8	Styrene	Mn(III)-C/MCM-41	4h	-78	89	92
9	Styrene (b)	Mn(III)-C/MCM-41	8 d	0	87	64
10	Styrene	Mn(III)-D	45min	-78	43	98
11	Styrene	Mn(III)-D/MCM-41	4h	-78	51	90
12	Styrene (b)	Mn(III)-D/MCM-41	7 d	0	47	51
13	Styrene	Mn(III)-E	45min	-78	54	88
14	Styrene	Mn(III)-E/MCM-41	4h	-78	61	80
15	α -Methylstyrene	Mn(III)-A	45min	-78	43	81
16	α -Methylstyrene	Mn(III)-A/MCM-41	4h	-78	56	74
17	α -Methylstyrene	Mn(III)-B	15min	0	51	98
18	α -Methylstyrene	Mn(III)-B/MCM-41	2h	0	59	67
19	α -Methylstyrene	Mn(III)-B/MCM-41	4h	-78	72	70
20	α -Methylstyrene	Mn(III)-C	45min	-78	43	90
21	α -Methylstyrene	Mn(III)-D	45min	-78	66	97
22	α -Methylstyrene	Mn(III)-E	45min	-78	69	92

Experimental details are provided in ref. 1. (a) Ee% was detrermined by GC. (b) 0.02 mol% catalyst

with homogeneous salen catalysts. In the case of styrene epoxidation, the salen complexes synthesized from diphenylethylenediamine derivative such as Mn(III)–(A) and –(C) were more efficient catalysts. Even though, the catalyst of Mn(III)–(C) has a half unit of salicylaldehyde, it gave a relatively high enantioselectivity. Furthermore, higher turnover number could be obtained over this unsymmetrical salen catalyst than over a symmetrical salen complex such as Mn(III)–(A,B). The highest turnover number achieved over heterogenized Mn salen/MCM-41 of (A) was 3200 in this work. Ito and Katsuki have reported that the new optically active (salen) Mn(III) complex having a carboxylate group on the ethylenediamine moiety was a very efficient catalyst for the asymmetric epoxidation of 2,2-dimethylchromene derivatives.[12] They have achieved a high level of turnover number (up to 9200) and enantioselectivity (up to 99% ee) using that non-symmetric salen Mn(III) complex. The pseudo-axially oriented carboxylate was postulated to coordinate to the Mn ion and the high enantioselectivity of the complex bearing a mono substituted diamine moiety was strongly related to the asymmetric induction by non-planarity of the salen ligand in that system. The high asymmetry-inducing ability of unsymmetrical salen complex in this work is attributed to the intense interaction of the substituent of salen ligands near the metal center with incoming substrate.

The increase in the enantioselectivity of catalyst (E) may be attributed to the presence of electrondonating methoxy groups. The immobilized chiral Mn salen/MCM-41 catalyst was also efficient in the epoxidation of α-methylstyrene. The Mn(III)–(B, D and E) catalyst synthesized from (+)-1,2-diaminocyclohexane derivative exhibited higher enantioselectivity than that obtained from (−)-1,2-diphenylethylenediamine for this reaction. Homogeneous chiral Mn(salen) complexes and the prepared solid samples were a dark brown color. After using Mn(salen) complexes immobilized on MCM-41 as catalysts, the resultant solution exhibited no color and no Mn was detected in the solution. This means that Mn(III) salen complexes immobilized on mesoporous materials are stable during the reaction and exist in the pore system without any extraction. The catalytic activity and selectivity of immobilized Mn(salen) complexes did not change, more or less, after four times of reusing. The catalyst could be reused after washing with CH_2Cl_2 solvent and drying under vacuum at 60°C.

In summary, new MCM-41 immobilized chiral (salen) complexes can be synthesized by a multi-step grafting method. The new chiral salen complexes of different structure were supported on mesoporous MCM-41 through the condensation of (3-aminopropyl) trimethoxysilane and 2,6-diformyl-4-*tert*-butylphenol. The asymmetric catalytic epoxidation using chiral (salen) complexes which are immobilized on MCM-41 can be applied with success and a high enantioselectivity is attainable in styrene and α-methylstyrene epoxidation. The chiral salen complexes immobilized on mesoporous material would be applied as an effective asymmetric heterogeneous catalyst.

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